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Formation constants of binary & ternary chelates of Ln(III) with maltol & kojic acid in presence of aminocarboxylic acids

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The formation constants of binary and ternary systems involving 3-hydroxy-2-methyl-4-pyrone (HMP) (maltol) and 5-hydroxy-2-hydroxymethyl-4-pyrone (HOMP) (kojic acid), with lanthanide metal ions [La(III), Pr(III), Nd(III), Gd(III), Dy(III) and Y(III)] in the presence of iminodiacetic acid (IMDA), hydroxyethyliminodiacetic acid (HIMDA) and nitrilotriacetic acid (NTA) have been determined in aqueous medium at 30°C and $\mu = 0.1$ *M* ($NaClO_4$). The order of stabilities of ternary systems is: HMP > HOMP and IMDA > HIMDA > NTA. These are explained in the light of the basicities of the ligands and charge neutralisation.

In continuation of our earlier studies[1] we report herein the formation constants of binary and ternary systems involving 3-hydroxy-2-methyl-4-pyrone (HMP, maltol) and 5-hydroxy-2-hydroxymethyl-4-pyrone (HOMP, kojic acid), with lanthanide metal ions [La(III), Pr(III), Nd(III), Gd(III), Dy(III) and Y(III)] in the presence of iminodiacetic acid (IMDA), nitrilotriacetic acid (NTA) and hydroxyethyliminodiacetic acid (HIMDA).

Maltol and kojic acid (Fluka), $NaClO_4$ (E. Merck), NTA and IMDA (Sigma) and HIMDA (Fluka) of AR grade were used as received. The proton-ligand formation constants of the ligands and the metal-ligand formation constants were determined *p*H-metrically using the Irving-Rossotti titration technique[2]. The formation constants of ternary systems have been evaluated by the method of Ramamoorthy and Santappa[3] in aqueous medium at 30°C and 0.1 *M* $NaClO_4$.

In binary systems the $\bar{n}$ values (0.1 to 1.9) indicate the formation of both 1:1 and 1:2 Ln(III)-L complexes (where L = HMP/HOMP). The metal-ligand formation constants evaluated by various computational techniques like half-integral, linear plots, pointwise calculations and method of least squares[4,5] are presented in Table 1. The stability order: La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III) > Y(III) is almost in accordance with the increasing charge/radius ratio of the metal ions[6].

The ternary complex formation is inferred from the non-superimposability of theoretical composite curve on the experimental curve in the region of mixed-ligand complex formation[5]. The ternary formation curve of Ln(III)-L-A coincides with Ln(III)-A curve (where A = HIMDA or NTA and L = HMP or HOMP] in the lower *p*H region and its divergence at higher *p*H region indicates the stepwise formation of the ternary complex. The ligand 'A' acts as primary ligand and the ligand 'L' as secondary ligand [equilibria (1) and (2)]

$$Ln^{3+} + A^{n-} \rightleftharpoons [Ln - A]^{(3-n)} \quad \ldots (1)$$

$$[Ln - A]^{(3-n)} + L^{-} \rightleftharpoons [Ln - A - L]^{(2-n)} \quad \ldots (2)$$

(where A = HIMDA or NTA and $n = 2$ for HIMDA and 3 for NTA).

In the case of ternary systems involving IMDA the ternary curve deviates from the beginning indicating the formation of the ternary complex in a simultaneous fashion [Eq. (3)]

$$Ln^{3+} + L^{-} + A^{2-} \rightleftharpoons [Ln - L - A] \quad \ldots (3)$$

The ternary formation constants are listed in Table 1. The ternary complexes [Ln − A − L] (where A = HIMDA/NTA and L = HMP/HOMP) formed in stepwise manner are less stable while those formed simultaneously [Ln − IMDA − HMP/HOMP] are more stable as compared to the binary complexes as revealed by $\Delta \log K$ values[7] (Table 1). The relative order of stabilities [La(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III) > Y(III)] is the same as that found for binary systems.

The stability order of ternary systems of HMP and HOMP follows the order of the basicities of these ligands, e.g. HMP > HOMP. The order of stability with respect to primary ligands is IMDA > HIMDA > NTA. This could be due to charge neutralisation in forming ternary complexes[7]. In the case of IMDA, coordination occurs with Ln^{3+} to form a neutral metal complex [Eq. (3)]; with HIMDA the coordination of $[HMP]^-$/$[HOMP]^-$ occurs with monopositive $[Ln - HIMDA]^+$ primary complex to form neutral complex whereas in the case of NTA, coordination between $[HMP]^-$/$[HOMP]^-$ and neutral primary complex [Ln − NTA] occurs to form a negatively charged complex [Eq. (2)]. Therefore greater electrostatic attraction may be expected (i) between Ln^{3+}, L[(HMP)/(HOMP)] and $[IMDA]^{2-}$; and (ii) between $[Ln - HIMDA]^+$ and L^- than between L^- and [Ln − NTA] complex.

Table 1—Binary and ternary formation constants* of maltol (L) and kojic acid (L') with aminocarboxylic acids [A^1 = IMDA; A^2 = HIMDA; A^3 = NTA] in aqueous medium

[I = 0.1 *M* $NaClO_4$; temp = 30°C]

log *K*	La(III)	Pr(III)	Nd(III)	Gd(III)	Dy(III)	Y(III)
$\log K^{M}_{ML}$	5.22	5.59	5.79	6.01	6.42	5.96
$\log K^{ML}_{ML_2}$	4.09	4.47	4.82	5.20	5.45	5.14
$\log K^{M}_{MA^1L}$	11.74	12.26	12.5	13.43	13.91	13.37
$\log K^{MA^1}_{MA^1L}$	(5.86)	(5.82)	(6.0)	(6.55)	(7.03)	(6.43)
$\Delta\log K$	0.64	0.23	0.21	0.74	0.61	0.67
$\log K^{MA^2}_{MA^2L}$	4.95	5.24	5.26	5.73	5.91	5.62
$\Delta\log K$	−0.27	−0.35	−0.53	−0.28	−0.51	−0.34
$\log K^{MA^3}_{MA^3L}$	4.08	4.36	4.69	5.15	5.30	4.85
$\Delta\log K$	−1.14	−0.96	−0.91	−0.61	−0.71	−0.78
$\log K^{M}_{ML'}$	5.03	5.15	5.23	5.38	5.72	5.32
$\log K^{ML'}_{ML'_2}$	3.98	4.5	4.61	4.96	5.13	5.01
$\log K^{M}_{MA^1L'}$	11.5	11.91	12.06	12.70	12.96	12.51
$\log K^{MA^1}_{MA^1L'}$	(5.61)	(5.47)	(5.56)	(5.74)	(6.23)	(5.83)
$\Delta\log K$	0.59	0.32	0.33	0.36	0.51	0.54
$\log K^{MA^2}_{MA^2L'}$	4.26	4.56	4.77	5.28	5.75	5.21
$\Delta\log K$	−0.77	−0.59	−0.46	−0.10	−0.07	−0.09
$\log K^{MA^3}_{MA^3L'}$	3.8	4.19	4.32	4.77	5.01	4.54
$\Delta\log K$	−1.14	−0.96	−0.91	−0.61	−0.71	−0.78

The values presented in parentheses are the stepwise formation constants evaluated from the simultaneous constants using Sigel's method[7].

*The deviations are within ± 0.03 log *K* units.

The distribution of metal among the various metal-ligand species was calculated using the computer program BEST[8]. The maximum percentage of mixed ligand complexes formed are 97%, 80% and 68% for La−HMP−IMDA, La−HMP−HIMDA and La−HMP−NTA species respectively and this is in accordance with the stabilities of mixed ligand complexes.

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